Photocatalytic Treatment of Cork Wastewater Pollutants. Degradation of Gallic Acid and Trichloroanisole using Triphenyl(thia)pyrylium salts

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ABSTRACT

The photocatalytic degradation of two typical pollutants present at the wastewaters of cork industry, namely gallic acid (GA) and 2,4,6-trichloroanisole (TCA) has been investigated using triphenylpyrylium (TPP^+) and triphenylthiapyrylium ($TPTP^+$) salts as organic photocatalysts. Fast removal of GA and slow but efficient degradation of the reluctant TCA were observed. The role of the transient species involved in the photodegradation has been investigated by means of photophysical experiments. Participation of singlet excited states was safely disregarded since lifetimes of both photocatalysts remained invariable upon addition of GA or TCA. Formation of photoactive ground state complexes was observed, and the complexation constants were estimated as $K_{TPP-GA} = 468.4\,M^{-1}$, $K_{TPP-TCA} = 528.0\,M^{-1}$ and $K_{TPTP-TCA} = 657.1\,M^{-1}$. Moreover participation of the triplet excited states in the electron transfer oxidation of GA was very efficient, while no reaction occurred from the triplet excited states in the case of TCA. In addition, thermodynamic calculations support the participation of the triplet excited state in the case of GA, while the lack of triplet quenching in the case of TCA is associated with a thermodynamically disfavored process. Overall, photophysical experiments indicate that for GA, oxidative electron transfer occurs mainly from the triplet excited state with marginal contribution of the ground state complexes, while for TCA formation of ground state complexes constitutes the only mechanistic pathway.

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1. Introduction

Water is an essential resource to life on Earth; thus, protecting the quality of water resources is doubtlessly one of the greatest challenges of sustainable development [1]. Moreover, to address the higher demand of good quality water availability by the increasing population, decontamination of wastewaters derived from the industrial activities is currently a subject of active research [2].

The elevate production of wine in Spain involves a parallel cork stoppers industry to guarantee the proper conservation of the product until consumption. However, the industrial production of cork stoppers includes a post-harvesting treatment of raw material with water at high temperatures to improve plastic properties. This results in a dark complex liquor containing not only suspended solids but also a high level of organic matter [3], in which phenolic and polyphenolic compounds are among the most representative pollutants [4,5]. This effluent exhibits low biodegradability,

thus, reducing the effectiveness of conventional biological treatments [6–8]. Nevertheless, advanced oxidation processes (AOPs) are promising alternatives that have demonstrated high efficiency for removal of reluctant organic contaminants [9].

The use of organic photocatalysis as appropriate AOPs to oxidize pesticides [10,11]. or emerging pollutants,[12–15] such as drugs in wastewaters effluents, has been widely reported. Organic photocatalysts exhibit absorption bands in the UV–visible region that can be excited to generate transient species that are able to interact with the pollutants [2]. Moreover, detection of these transient excited states or reactive intermediates by time-resolved techniques (emission, transient absorption spectroscopy, etc.) provides a powerful tool to investigate the involved reaction mechanisms. In this context, triphenylpyrylium (TPP^+) and triphenylthiapyrylium ($TPTP^+$) salts have been employed [10,15–18] due to their capability to produce photocatalytic degradation of pollutants *via* oxidative electron transfer [19].

With this background, the aim of this work is to investigate the photocatalytic degradation of two typical pollutants present at the wastewaters of cork industry, namely gallic acid (GA) and 2,4,6-trichloroanisole (TCA) (see Fig. 1), using TPP^+ and $TPTP^+$ as organic photocatalyst. Different mechanisms will be postulated to explain
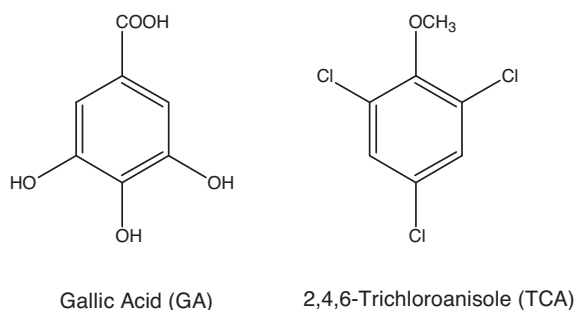
Fig. 1. Chemical structures of the selected cork wastewater pollutants.

the photodegradation of each pollutant on the basis of the transient species involved.

2. Experimental

2.1. Reagents

Gallic acid (GA), 2,4,6-trichloroanisole (TCA), 2,4,6-triphenylpyrylium (TPP$^+$) tetrafluoroborate salt, 2-nitrobenzoic acid, pentadecane and acetonitrile were obtained from Aldrich.

2,4,6-Triphenylthiapyrylium (TPTP$^+$) perchlorate was obtained from TPP$^+$ as described previously [20]. Briefly, a solution of TPP$^+$ (0.50 g) in acetone (23.6 mL) was treated with aqueous sodium sulphide (10% w/w, 1.97 mL) until the mixture turned red-coloured. Then, perchloric acid (20% w/w, 5.9 mL) and water (23.6 mL) were added to precipitate the TPTP$^+$ salt as a yellow powder. Then, the solid was filtered, washed with water and purified by re-precipitation from acetone-ether.

2.2. Photochemical reactions

Photochemical reactions were performed in Pyrex glass vessels with magnetic stirring using a Luzchem photoreactor (model LZC-4 V). Unless otherwise stated, vessels were loaded with 100 mL of acetonitrile solutions of the pollutants GA or TCA (5 mg/L) and photocatalysts TPP+ or TPTP+ (10 mg/L). The pollutant:photocatalyst molar ratio (1:1) was chosen to optimize the absorption of photons and reduce irradiation times. Internal standards, 2-nitrobenzoic acid or pentadecane (5 mg/L), were added to monitor photodegradation of GA or TCA, respectively. Irradiations were performed under N$_2$ or air as indicated.

Aliquots were taken at different irradiation times, and the removal of GA or TCA was monitored by HPLC or GC, respectively. The HPLC was a Varian 240 model with quaternary pump 9012Q, photodiode detector DAD 9065 and wavelength detection from 200 to 360 nm. A Mediterranea Sea 18 column (25 mm × 0.46 mm, 5 μm particle size) was employed. The mobile phase was an isocratic mixture of water pH 3 (50%) and acetonitrile (50%) at the flow rate of 0.7 mL/min; the detection wavelength was fixed at 275 nm. UPLC-MS-MS was performed on an ACQUITY UPLC system (Waters Corp.) with a conditioned autosampler at 4 °C. The separation was carried out on an ACQUITY UPLC BEH C18 column (50 mm × 2.1 mm i.d., 1.7 μm). The Waters ACQUITY™ XevoQToF Spectrometer (Waters Corp.) was connected to the UPLC system via an electrospray ionization (ESI) interface. The ESI source was operated in negative ionization mode with the capillary voltage at 3.0 kV. The GC equipment was a Bruker instrument 430–GC equipped with a ZB50 (30 m × 0.25 mm × 0.5 μm) column with stationary phase of 5% of alternated phenylmethyl silicone. The GC–MS analyses were carried out in an Agilent 6890N equipped with a HP-5MS (30 m × 0.25 mm × 0.5 mm) column and a 5973 network mass selective detector.

2.3. Photophysical instrumentation

Quartz cells of 1 cm optical path length were employed for all photophysical measurements, which were run at room temperature under air (steady-state and time-resolved fluorescence) or nitrogen (laser flash photolysis).

Absorption spectra (UV/Vis) were performed on a Shimadzu UV-2101PC spectrometer. Steady-state fluorescence spectra were recorded on a FS900 fluorometer, and time-resolved fluorescence experiments were measured in a FL900 setup, both from Edinburgh Instruments. Lifetime measurements were based on single-photon-counting using a hydrogen flash-lamp (1.5 ns pulse width) as excitation source. The kinetic traces were fitted by mono-exponential decay functions using a re-convolution procedure to separate them from the lamp pulse profile.

Laser flash photolysis (LFP) studies were carried out with a pulsed Nd: YAG SL404G-10 Spectron Laser Systems at the excitation wavelength of 355 nm. The single pulses were ∼10 ns duration, and the energy was lower than 15 mJ pulse^{-1}. The detecting light source was a pulsed Lo255 Oriel Xenon lamp. The laser flash photolysis system consisted of the pulsed laser, the Xe lamp, a 77,200 Oriel monochromator, an Oriel photomultiplier tube (PMT) housing and a 70,705 PMT power supply. The oscilloscope was a TDS-640A Tektronix. The output signal from the oscilloscope was transferred to a personal computer.

2.4. Photophysical experiments

For the steady-state and time-resolved fluorescence experiments, increasing concentrations of pollutants (up to 1.6×10^{-3} M or 1.1×10^{-3} M for GA or TCA, respectively) were added to solutions of TPP$^+$ or TPTP$^+$ (with absorbance 0.1 at the irradiation wavelength of 410 nm and 365 nm for TPP$^+$ and TPTP$^+$, respectively).

Job's plot experiments were performed to investigate the stoichiometry of the [Photocatalyst$^{\delta+}$ – Q$^{\delta'+}$] complexes. The absorbance changes were measured at 406 nm and plotted against the pollutant molecular fraction, keeping constant the total concentration of pollutant and photocatalyst (1×10^{-5} M).

For the laser flash photolysis experiments, increasing amounts of pollutant (up to 7×10^{-5} M for GA and TCA) were added to solutions of 7×10^{-5} M of TPP$^+$ or TPTP$^+$, under N$_2$ atmosphere.

3. Results and discussion

3.1. Photochemical degradation

The efficiency of the homogeneous photocatalysts TP(T)P$^+$, acting usually *via* electron transfer mechanism [19], in the degradation of GA and TCA was evaluated in organic media under N$_2$ and air, using lamps centred at 420 nm to ensure selective excitation of TP(T)P$^+$. For consistency, the same solvent was used for the photodegradation studies and for the mechanistic experiments (see Sections 3.2–3.5). Hence, in order to avoid possible interferences from aggregation phenomena and hydrolysis of the photocatalyst, acetonitrile was selected as the solvet of choice. From the data shown in Fig. 2A and B complete removal of GA was observed in less than one hour, while TCA was more reluctant to degradation; in fact 90% of TCA removal was only found after 50 hours using TPTP$^+$ under air. Moreover, in the case of TCA, where long irradiation times were needed, the reaction rate decreased considerably after 10 h. This effect, due to the partial solvolysis of the central heterocyclic ring of the photocatalysts, has been observed previously and could eventually be circumvented upon adsorption onto inorganic supports [17]. Photodegradation of pollutants was more efficient under air using either TPP$^+$ or TPTP$^+$; however, while TPP$^+$
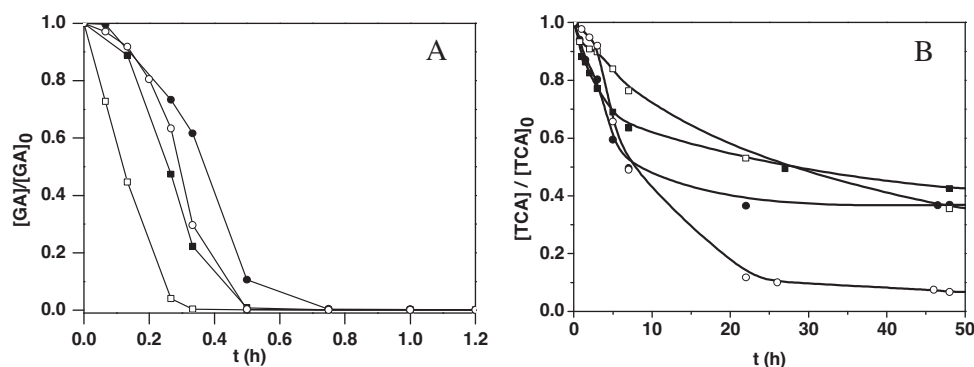
Fig. 2. Plot of the relative [GA] (A) or [TCA] (B) upon irradiation times using TPP$^+$ under air (□) or N$_2$ (■), or TPTP$^+$ under air (○) or N$_2$ (●) as photocatalysts (λ_{exc} = 420 nm), monitored by HPLC (GA) or GC (TCA). [GA]$_0$ = [TCA]$_0$ = 5 mg/L, [TP(T)P$^+$]$_0$ = 10 mg/L.
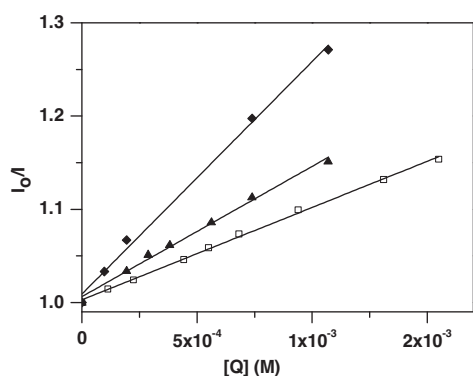

Fig. 3. Stern-Volmer plots obtained for the steady-state fluorescence quenching of TPP$^+$ by GA (□) and TCA (▲) and TPTP$^+$ by TCA (♦) in aerated acetonitrile solutions (λ_{exc} = 405 nm).
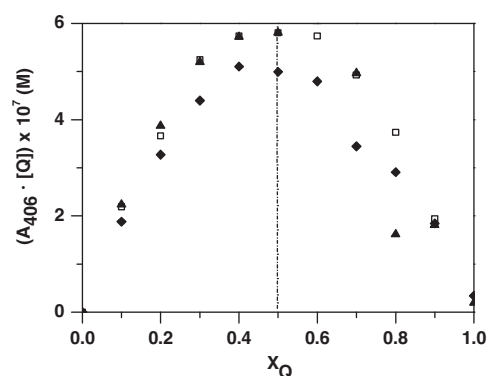
Fig. 4. Job's plots for the absorption of TPP$^+$ *versus* GA (□) or TCA (▲) and TPTP$^+$ *versus* TCA (♦) molar fractions, at total concentration ([TP(T)P$^+$] + [Q]) of 1×10^{-5} M.

was more efficient in the photodegradation of GA, TPTP$^+$ gave higher removal yields in the case of TCA. For comparison, parallel experiments were performed in aerobic aqueous media. Again GA reacted faster than TCA, but longer irradiation times were needed to achieve similar conversions. Mass spectral analysis of the complex photolysis mixtures revealed formation of minor amounts of decarboxylation and oxygenation products from GA, while in the case of TCA the only identified product was 3,4,5-trichlorophenol. Control experiments to determine the extent of direct photolysis were carried out in the absence of photocatalyst. Under these conditions, no significant degradation was observed after 1 h (in the case of GA) or 60 h (in the case of TCA). Although both photocatalysts act *via* electron transfer, the specific species responsible for the degradation has to be determined in each particular case. Examples of participation of ^{1}TPP^{+*} [17], ^{3}TPP^{+*} [15], or a non-emissive ground state complex [10] in the removal of pollutants can be found in the literature. Analogously, despite the high intersystem crossing quantum yield for TPTP$^+$ (Φ_{ISC} = 0.93)[2] involvement of ^{1}TPTP^{+*} was proposed in the photodegradation of pyrimethanil or alachlor [21]. Therefore, it looked necessary to perform a full mechanistic analysis of the participation of the singlet or triplet excited states of TP(T)P$^+$, or even ground state complexes in the degradation of the selected cork wastewater contaminants.

3.2. Fluorescence quenching studies

First, steady-state fluorescence experiments were performed to investigate the participation of the singlet excited state and/or the ground state of TP(T)P$^+$ in the photodegradation of GA and TCA. Hence, a decrease in the emission of TPP$^+$ was observed upon addition of increasing concentrations of GA or TCA, while the emission

of TPTP$^+$ only decreased with the addition of TCA, keeping constant upon increasing concentrations of GA. Relative emission of TP(T)P$^+$ was plotted against pollutant concentration (Fig. 3). By application of the Stern–Volmer relationship, using the reported singlet lifetime of TP(T)P$^+$ (4.2 ns) [22], the corresponding quenching rate constants were determined: 2.4×10^{10}, 3.3×10^{10} and 5.9×10^{10} M^{-1}s^{-1}, for the quenching of TPP$^+$ by GA or TCA and TPTP$^+$ by TCA, respectively. Next, time-resolved fluorescence experiments were also performed to determine the real participation of the singlet excited states of TP(T)P$^+$ in the photodegradation of the contaminants; however, singlet lifetimes of both photocatalysts remained invariable upon addition of GA or TCA. This fact, together with the determined values for the steady-state quenching rate constants, above the diffusion rate in CH$_3$CN (k_{diff} = 1.9×10^{10} M^{-1} s^{-1}) [23], clearly disregarded the participation of the singlet excited states and pointed to the formation of ground-state complexes as the species responsible, at least in part, for the observed fluorescence quenching.

3.3. Formation of ground state complexes

The stoichiometry of the purported complexes was determined from Job's plot experiments [24,25], Thus, UV–vis spectra of solutions containing different molar fractions of photocatalyst and pollutant at a constant total concentration of 1×10^{-5} M were recorded. Then, the UV absorption (at 406 nm) was plotted against the molar fraction of the pollutant, and a curve was obtained in the three cases. The maxima of these parabolas was found at $X_{pollutant}$ = 0.5, which corresponds to a 1:1 stoichiometry (Fig. 4).
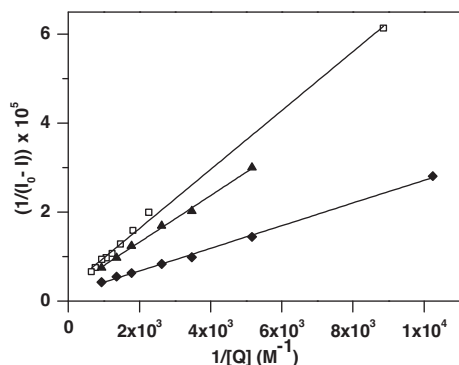
Fig. 5. Benesi–Hildebrand relationships for TPP⁺ complex formation with GA (□) or TCA (▲) and TPTP⁺ with TCA (♦).

$$TP(T)P^+ + Q \leftrightarrows [TP(T)P^{\delta+} - Q^{\delta'+}]$$

$$K = \frac{\left[TP(T)P^{\delta+} - Q^{\delta'+}\right]}{[TP(T)P^+][Q]} \qquad \text{Eq. 1}$$

Where Q represents the quencher (GA or TCA) and K is the complexation constant, which could be determined from the Benesi-Hildebrand relationship: [26,27].

$$\frac{1}{I_o - I} = \frac{1}{I_o - I_1} + \frac{1}{(I_o - I_1)K[Q]} \qquad \text{Eq. 2}$$

Where I_0 and I are the emission intensities of each photocatalyst in the absence of pollutant and after every addition, respectively. The complexation constants were obtained from the slopes and intercepts of each fitting (Fig. 5), and the determined values were: $K_{TPP-GA} = 468.4\,M^{-1}$, $K_{TPP-TCA} = 528.0\,M^{-1}$ and $K_{TPTP-TCA} = 657.1\,M^{-1}$.

3.4. Transient absorption spectroscopy

The potential involvement of the triplet excited state of TP(T)P⁺ in the degradation of the pollutants was evaluated by laser flash photolysis (LFP) experiments. Thus, excitation ($\lambda_{exc} = 355$ nm) of deaerated solutions of TP(T)P⁺ in acetonitrile led to a broad absorption band (400–600 nm) in the case of TPP⁺ and a sharp band centred at 470 nm for TPTP⁺, associated with the triplet state of both photocatalysts [2,19]. Then, the lifetime of the triplets (at 470 nm and 620 nm for TPP⁺ and TPTP⁺, respectively) was determined upon addition of increasing concentrations of the pollutants.

Fig. 6A and B shows a decrease in the lifetime of triplet excited states of both photocatalysts, upon increasing concentrations of GA.
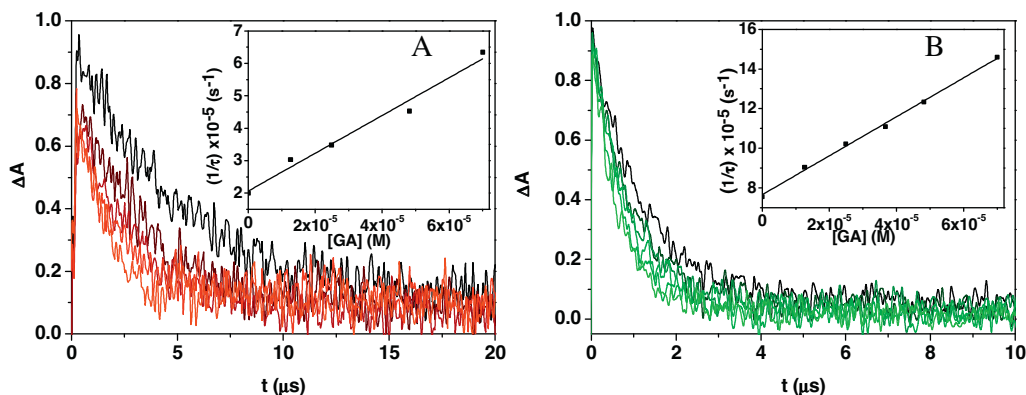
The corresponding quenching constants were determined from the Stern Volmer linear relationships:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_q[Q] \qquad \text{Eq. 3}$$

where τ is the triplet excited state lifetime after each addition, τ_0 is the triplet excited state lifetime before the additions and [Q] is the concentration of contaminant in the sample after each addition. Thus, the determined values were: $k_q = 5.8 \times 10^9\,M^{-1}\,s^{-1}$ and $9.8 \times 10^9\,M^{-1}\,s^{-1}$ for the quenching of $^3(TPP^+)^*$ and $^3(TPTP^+)^*$, respectively. As a further evidence for the electron transfer process, the spectrum of TPP⁺ in the presence of GA (7×10^{-5} M) was recorded upon LFP, and a band centred at 550 nm corresponding to the semireduced pyranyl radical (TPP·) was observed instead of the initial $^3(TPP^+)^*$ (Fig. 7).

In the case of TCA, addition of growing amounts of pollutant did not have any effect on the lifetimes of $^3(TPP^+)^*$ or $^3(TPTP^+)^*$, indicating that no reactions occurs from the triplet excited states. Nevertheless, the transient absorption spectra recorded immediately after the laser pulse revealed the presence the presence of TCA·⁺ peaking at ca. 460 and 500 nm (see Fig. 7B for the case of TPP⁺ where the pyranyl radical is also detected at 550 nm).

3.5. Thermodynamics of photoinduced electron transfer

The feasibility of a photoinduced electron transfer from GA to the triplet excited state of TP(T)P⁺ was evaluated using the Rehm–Weller equation: [28].

$$G\left(kcal\,mol^{-1}\right) = 23.06\left[E_{ox}(Q) - E_{red}(TP(T)P^+)\right] - E_T^*(TP(T)P^+) \qquad \text{Eq. 4}$$

The values for $E_{red}(TP(T)P^+)$ and $E_T^*(TP(T)P^+)$ were taken from the literature (-0.29 V vs. SCE and 52 kcal mol⁻¹, respectively) [2,19,29,30]. Using the reported E_{ox}(GA) of +0.80 V (vs. SCE) [16], the estimated ΔG to $^3TP(T)P^*$ was −27 kcal mol⁻¹ indicating that electron transfer is indeed exergonic. For TCA, the lack of triplet quenching could be associated with a thermodynamically disfavored process. According to (Eq. 4), this would be the case for a E_{ox} value above 2.0 V. As a matter of fact, no literature value has been found for this parameter, by contrast with the easy availability of E_{red} data [31].

3.6. Mechanistic proposal

Photodegradation of the pollutants GA and TCA in the presence of TP(T)P⁺ has indeed been achieved, with higher reactions rates in the case of GA. A mechanistic proposal, which accounts for all the experimental observations, is outlined in Scheme 1. The
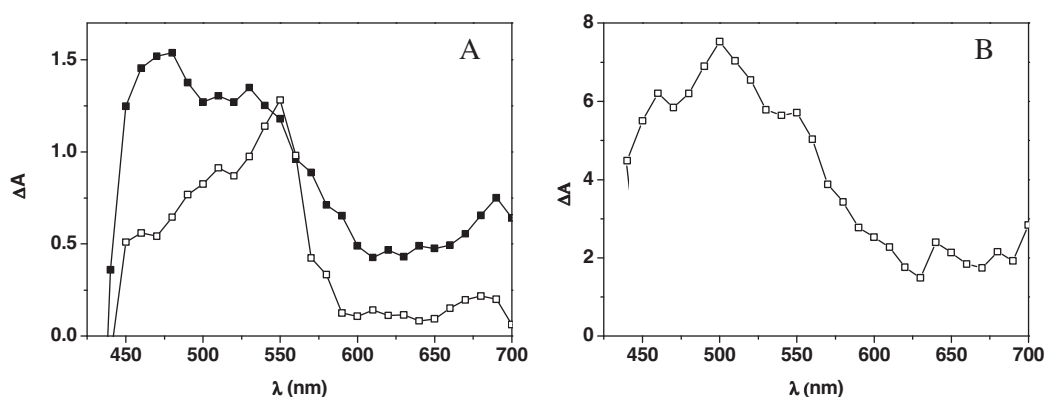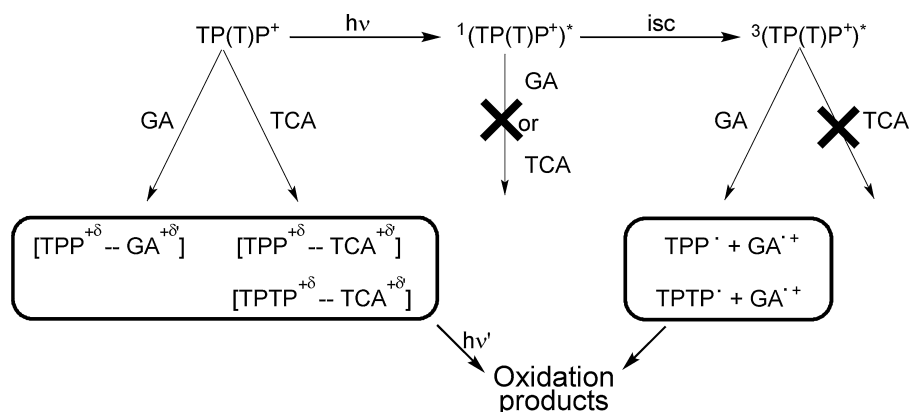

Fig. 6. Kinetic traces obtained upon irradiation ($\lambda_{exc} = 355$ nm) of deaerated acetonitrile solutions (7×10^{-5} M) of TPP⁺ (A) or TPTP⁺ (B) in the presence of increasing concentrations of GA ($0–7 \times 10^{-5}$ M), recorded at 470 nm (A) or 620 nm (B). Insets: Stern–Volmer plots for the reverse of TPP⁺ (A) or TPTP⁺ (B) triplet lifetime *vs.* GA concentration.

Fig. 7. Transient absorption spectra obtained upon laser flash photolysis of deaerated acetonitrile solutions of TPP$^+$ (7×10^{-5} M) in the absence (■) and in the presence (□) of GA (7×10^{-5} M) (A) and in the presence (□) of TCA (7×10^{-5} M) (B) recorded 2.4 μs after the pulse.

Scheme 1. Mechanistic proposal for the photodegradation of GA and TCA using TP(T)P$^+$ as organic photocatalysts.

active participation of the singlet excited states of TP(T)P$^+$ can be safely ruled out, since no changes in their fluorescence lifetimes were observed in the presence of the pollutants. Nevertheless, formation of ground-state complexes between the photocatalysts and the pollutants was demonstrated for TPP$^+$ with GA or TCA and for TPTP$^+$ with TCA (from the steady-state fluorescence quenching and Job's plot experiments). The determined equilibrium constant values from the Benesi–Hildebrand analysis were: $K_{\text{TPP-GA}} = 468.4\,\text{M}^{-1}$, $K_{\text{TPP-TCA}} = 528.0\,\text{M}^{-1}$ and $K_{\text{TPTP-TCA}} = 657.1\,\text{M}^{-1}$. In addition, the decrease in the triplet lifetime of ^{3}TP(T)P* upon addition of GA, together with the formation of the pyranyl radical, pointed to the active participation of this excited species in the photodegradation of GA. Thermodynamic calculations also support the participation of the triplet excited state in this case.

The relative contribution of complex formation and triplet quenching for the degradation of GA by TPP$^+$ was estimated on the basis of the concentrations used ([GA] = 5 mg/L and [TPP$^+$] = 10 mg/L), the complexation constant ($K_{\text{TPP-GA}} = 468.4\,\text{M}^{-1}$), the triplet lifetime ($\tau_\text{T} = 4.8\,\mu\text{s}$) and the determined triplet quenching constant ($k_\text{q} = 5.8 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$). Under these conditions, only 1.4% of the initial TPP$^+$ is employed in the formation of the purported complex, while ca. 27% of the initially excited TPP$^+$ follow the electron transfer pathway from the triplet excited state.

4. Conclusions

Photocatalytic treatment of two representative cork wastewater pollutants in the presence of (thia) pyrylium salts as organic photocatalysts reveals fast removal of gallic acid and slow but efficient degradation of the reluctant 2,4,6-trichloroanisole. Photo-

physical experiments indicate that for gallic acid, oxidative electron transfer occurs mainly from the triplet excited state, while for 2,4,6-trichloroanisole formation of ground state complexes constitutes the only mechanistic pathway.

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